Gas Generating Mixtures

BACKGROUND AND SUMMARY OF THE INVENTION

The subject matter of the present invention is a method for the production of gas generating mixtures, as well as the gas generating mixtures which can be produced thereby.

Gas generators are being used increasingly for life saving purposes, for example in vehicles. Up to a few years ago it was common to use sodium azide in the gas generating mixtures used in these gas generators. Sodium azide is toxic and can easily react with heavy metals such as copper and lead to form extremely dangerous and violently reactive compounds. Therefore, special precautions must be taken in the production of the raw material, the gas mixture, in its processing and in quality control. For this reason also the disposal of the sodium azide, for example when defective gas generators are replaced, or in the scrapping of the vehicles, presents a special problem. Also, improper use must be reliably prevented.

German Patent Application DE 195 05 588 A1 describes gas charges which contain no sodium azide but do contain nitrogen compounds (fuels) from the group of the tetrazoles, triazoles, triazines, cyanic acid, ureas, and their derivatives or their salts. The oxidizers are as a rule three compounds which are derived from peroxides, nitrates and perchlorates. Components are used as combustion moderators which are able to affect the burning and its rate by heterogeneous or homogeneous catalysis.

To an increasing extent, pollution within the vehicle is simulated in order to avoid insurance claims. One such test is a temperature shock test with numerous cycles in a

temperature range from -35 to +85 °C. In many cases intolerable variations in the strength of the tablets occur in the known gas generating mixtures.

When potassium compounds are used, and especially perchlorates, when the mixture burns potassium chloride forms, which since it is finely divided may lead to adverse reactions in vehicle occupants who have allergic tendencies (asthmatics).

Measures for improving the homogeneity of a mixture with components of very fine grain size, for example by grinding the components together or by comminution after distributing them by moistening with water, cannot be used in the presence of perchlorates for reasons of safety. Such methods are a requirement for satisfying the strict requirements concerning the composition of smoke and gases produced by explosions.

It was the purpose of the present invention to eliminate these disadvantages of the state of the art.

The problem on which the invention is based has been solved by a method for the production of gas generating mixtures with the features of the principal claim, and by the gas generating mixtures which can be prepared by this method. Preferred embodiments of the solution according to the invention are specified in the subordinate claims.

DETAILED DESCRIPTION

The known gas charges are prepared in a manner known in itself. This can be explained by way of example by the gas charges in DE 195 05 568 A1. The components are, for example, mixed, dried, screened, divided into portions and compressed to form tablets. The burning rate can be set by the shape and size of the grains, for example by

crushing and screening out the fragments of the bulk material obtained. The bulk material can be produced in great quantity and adapted to the particular burn requirements by mixing fractions of different dynamic volatility. Also, premixes of two or three components can be used in order to enhance safety or to improve the result produced by the mix.

A mixture of oxidizing agent and additives can be prepared, for example, before it comes in contact with the nitrogenous compounds. The mixture, however, can also be made by kneading components moistened with water and then granulating the mixture, e.g., by pressing through sieves, by extrusion, or the like. At the same time binding agents, such as water glass, inorganic rubber (phosphorus nitrile chloride) or also small amounts of organic binders such as acrylic resins, PTFE, or guar gum can be added.

As described by way of example for these gas charges, gas generating mixtures are prepared as a rule by the mere mixing together of previously treated components. Intimate homogeneity of the components with one another cannot be achieved in this manner, so that not rarely the mixtures thus made have disadvantages, for example when it is important to satisfy stringent requirements regarding the composition of smoke and gases resulting from explosions. The intimate homogeneity required for the satisfaction of these requirements cannot be assured by the mere mixing of the components. The technique used in other fields, of preparing mixtures of different components by grinding these components together, could not be applied heretofore to the production of gas-generating mixtures on account of the greater threat to safety.

Surprisingly it has been found that certain components, in some cases already known as

friction agents, burn moderators, or also as oxidizers, can serve as passivators, so that the components of the gas generating mixtures can be ground together in appropriate apparatus such as ball mills or pinned disk mills, for example. In the presence of these passivators, for example, nitroguanidine fuel and the alkali nitrate oxidizers can be ground, together with other additives if desired, in a ball mill or pinned disk mill, without danger, down to an average grain size of <20 μm. By this grinding process an especially intimate homogenization of the components with one another can be achieved. The components are mixed with special homogeneity if they are ground to an average grain diameter of 10 to 15 μm. Depending on what average grain diameter the starting components have, the desired intimate homogeneity of all components that is necessary for the application can be achieved through the corresponding grinding time. In this manner, average grain diameters of even <5 μm can be attained.

Components serving as passivators in this sense are the friction agents known and used as such in gas generating mixtures, as well as components which are used in gas-generating mixtures in order to influence the burning of the gas-generating mixture and its speed. Such components, also called burn moderators, and substances used as passivators in the grinding process in the meaning of the present invention, are metals, metal oxides and/or metal carbonates and/or metal sulfides. Boron, silicon, copper, iron, titanium, zinc or molybdenum can be used with preference as metals. Calcium carbonate can also be used. Sulfur, boron, silicon or ferrocene and its derivatives are likewise suitable. Mixtures of these passivators can likewise be used. These components acting as passivators in the

grinding process in the meaning of the invention are vaporized to the gas phase by the temperatures occurring in the reaction taking place in the gas generator and can thus enter into the reaction as burn moderators themselves or as secondary products.

The components are intimately and effectively mixed when specific friction agents are used as passivators, for example iron oxide, aluminum oxide, preferably basic aluminum oxide, tin dioxide or titanium dioxide.

Also the components, tungsten trioxide, cerium-IV oxide, ammonium cerium nitrate and/or luteonitrate, which are used as oxidizers, can be used as passivators in the meaning of the invention. When these substances are used as oxidizers, therefore, a portion of the oxidizer itself functions as a passivator.

The content of passivators in the mixture is governed ultimately by the necessary degree of passivation, and can amount to between 1 and 15 wt.-% in the mixture. The homogeneous gas-generating mixture that can be made in this manner according to the invention can then be compressed in a manner known in itself. If a granular product is desired, the compacts are broken up and sorted then by sifting into the desired grain sizes.

The gas-generating mixtures that can be prepared according to the invention can contain as fuel nitrogenous compounds from the group of the tetrazoles, triazoles, triazines, cyanuric acid, and ureas and their derivatives or salts or mixtures thereof. Preferred are the tetrazole derivatives 5-aminotetrazole, lithium-, sodium-, potassium-, zinc-, magnesium-, strontium- or calcium-5-aminotetrazolate, 5-aminotetrazole nitrate or sulfate or perchlorate and similar compounds, 1-(4-aminophenyl)-tetrazole, 1-(4-nitrophenyl)-tetrazole, 1-methyl-5-

dimethylaminotetrazole, 1-methyl-5-methylaminotetrazole, 1-methyltetrazole, 1-phenyl-5-aminotetrazole, 1-phenyl-5-hydroxytetrazole, 1-phenyltetrazole, 2-ethyl-5-aminotetrazole, 2-methyl-5-aminotetrazole, 2-methyl-5-carboxyltetrazole, 2-methyl-5-methylaminotetrazole, 2-methyltetrazole, 2-phenyltetrazole, 5-(p-tolyl)-tetrazole, 5-diallylaminotetrazole, 5-dimethylaminotetrazole, 5-ethylaminotetrazole, 5-hydroxytetrazole, 5-methyltetrazole, 5-methylaminotetrazole, 5-n-decylaminotetrazole, 5-n-heptylaminotetrazole, 5-n-octylaminotetrazole, 5-phenyltetrazole, 5-phenylaminotetrazole or bis-(aminoguanidin)-azotetrazole and diguanidinium-5,5′-azotetrazolate, as well as 5,5′-bitetrazole and its salts, such as the 5,5′-bi-1H-tetrazole ammonium compounds. 1,3,5-triazine is used as a triazine derivative, 1,2,4-triazole-5-one and 3-nitro-1,2,4-triazole-5-one as triazole derivatives, sodium cyanate, cyanuric acid, cyanuric acid ester, cyanuric acid amide (melamine), 1-cyanoguanidine, sodium dicyanamide, disodium cyanamide, dicyandiamidine nitrate, dicyandiamidine sulfate are used as cyanic acid derivatives, and biuret, guanidine, nitroguanidine, guanidine nitrate, aminoguanidine, aminoguanidine nitrate, thiourea, triaminoguanidine nitrate, aminoguanidine hydrogen carbonate, azodicarboxylic acid diamide, tetrazene, semicarbazide nitrate and urethanes, ureides such as barbituric acid and their derivatives are used as urea derivatives. Nitroguanidine or 5-aminotetrazole are used as especially preferred components. Used as derivatives of 5-aminotetrazole are the salts thereof in which the acidic hydrogen atoms on the 5-aminotetrazole are replaced salt-like by toxicologically unobjectionable elements such as calcium, magnesium or zinc. However, compounds are also usable in which the cation is formed from ammonium, and from

guanidinium and its amino derivatives. The content of these fuels in the mixture is from 5 to 70 wt.-%, preferably 10 to 55 wt.-%.

Nitrates, preferably ammonium nitrate, nitrates of the alkali or alkaline earth metals, especially lithium nitrate, sodium nitrate, potassium nitrate or strontium nitrate are used as oxidizing agents, as well as iron oxide, preferably in an especially fine grain size distribution. Additional oxidizing agents can be tungsten trioxide, cerium-IV oxide, ammonium cerium nitrate and/or luteonitrate. Mixtures of these oxidizing agents can likewise be used.

Furthermore, the mixture according to the invention for gas generation can contain the usual additives, for example those which are able to reduce the content of harmful gases such as nitrogen oxides and/or carbon monoxide, or pressing, spreading, flowing adjuvants or binders.

To increase the strength of the compacts, these additives can also contain fibers, as well as agents producing porosity to control the burning.

As a binder, for example, an agent can be used which as such, by thermoplastic deformation or after activation with a suitable solvent, e.g., by immersion, spraying or in a solvent vapor, contributes to the strength of the compacts. In addition to the use of a binding agent in the gas charge mixture, the tablets can also be coated on their exterior with a binder. This is done by immersion or spraying with a binder dissolved in a solvent. In this manner the following can be achieved:

– reduction of surface attrition

- better sliding properties of the tablets
- increase of tablet strength
- resistance to environmental influences.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The following examples are intended to further explain the invention, without limiting it:

Examples 1 to 5:

Test No.	Nitroguanidine wt.-%	Potassium nitrate wt.-%	Iron oxide wt.-%	Aerosil wt.-%	Boron nitride wt.-%
1	51.5	41.5	5	1.5	0.5
2	51	41	5	2.5	0.5
3	51.5	42	5	1.0	0.5
4	51.5	42.5	4	1.5	0.5
5	51.5	42.2	5	0.8	0.5

Tests in the Ballistic Bomb

In each case 2.5 g of the gas-generating mixture of examples 1 to 5 were tested in the ballistic bomb. The results are given in the following table:

Test No.	Tablet Geometry	Pmax [bar]	Δt 40-60% [ms]
1	diam. 3 x 2 mm	648	2.50
2	diam. 3 x 2 mm	556	3.48
3	diam. 3 x 2 mm	590	2.40
4	diam. 3 x 2 mm	571	3.05
5	diam. 3 x 2 mm	595	2.22

Test No.	Tablet Geometry	Pmax [bar]	Δt 40-60% [ms]
1	Diam. 4 x 1.5 mm	610	3.20
2	Diam. 4 x 1.5 mm	585	3.85
3	Diam. 4 x 1.5 mm	600	2.50
4	Diam. 4 x 1.5 mm	565	3.25
5	Diam. 4 x 1.5 mm	624	2.38

Thermodynamic Characteristics

Test No.	Explosion Heat (J/g)	Combustion temp. (K)	CO calculated (%)	CO measured in 2.5 m3 (ppm)	NOX_x calculated (%)	NOx measured in 2.5 m^3 (ppm)
1	3772	2373	≤0.0001	23	<< 0.0001	1.5
2	3772	2362	≤0.0001		<< 0.0001	
3	3761	2341	≤0.0001		<< 0.0001	
4	3736	2328	≤0.0001		<< 0.0001	
5	3768	2327	≤0.0001		<< 0.0001	